

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 321 307 B1

(12)

EUROPEAN PATENT SPECIFICATION

- (45) Date of publication of patent specification: **21.04.93** (51) Int. Cl.⁵: **C10G 67/04**
- (21) Application number: **88311989.3**
- (22) Date of filing: **16.12.88**

(54) Method for isomerizing wax to lube base oils.

(30) Priority: **18.12.87 US 135150**

(43) Date of publication of application:
21.06.89 Bulletin 89/25

(45) Publication of the grant of the patent:
21.04.93 Bulletin 93/16

(54) Designated Contracting States:
BE DE ES FR GB IT NL

(56) References cited:
BE-A- 627 517
FR-A- 1 457 131
US-A- 2 668 866

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EP 0 321 307 B1

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Description

The present invention relates to a method of isomerizing wax to lube base oil.

- US-A-3308052 describes and claims a method for upgrading a waxy hydrocarbon mixture containing less than about 50 percent of distillate oil to lower boiling products comprising jet fuels and high VI lube oils which comprises contacting the waxy material with hydrogen in the presence of a hydroisomerizing catalyst under hydroisomerizing conditions to obtain a conversion of said waxy hydrocarbon to products boiling below about 650° F (343.3° C) of from about 25 percent to about 70 percent, separating the hydroisomerized product under conditions to obtain a jet fuel boiling range product and a liquid product boiling above about 650° F (343.3° C), cooling the liquid product boiling above about 650° F (343.3° C) to a temperature below about 20° F (-6.7° C) and recovering a high viscosity index lube oil from the product of the cooling step.

- US-A-2668866 describes and claims a process for the production of a lubricating oil having low pour point and high viscosity index from paraffin wax which comprising vaporizing a normally solid paraffin wax with recycle gas containing at least one mole of hydrogen per mole of said wax, contacting the mixture completely in the vapor phase with a supported platinum catalyst at a temperature between about 375° C and about 490° C and under a pressure between about 50 and 3000 p.s.i. (0.345 and 20.69 MPa) for a time between 0.5 second and 25 seconds insufficient to produce more than 25% conversion to cracked products of lower molecular weight, cooling the gaseous product, separating and recycling the hydrogen-containing gas, distilling from the product the small amount of normally liquid cracked products, and subjecting the remainder to a dewaxing treatment to separate the normally liquid oil having the designated properties.

FR-A-1457131 and corresponding GB-A-1065205 disclose and claim a process for the production of lubricating oils or lubricating oil components from petroleum waxes, which comprises the steps:

- (1) isomerizing a petroleum wax in the presence of hydrogen in a first zone over a catalyst containing a hydrogenation-dehydrogenation component and a solid acid-acting refractory support;
- (2) isomerizing at least the portion boiling in the lubricating oil boiling range of the effluent from the first zone in the presence of hydrogen over a catalyst containing a hydrogenation-dehydrogenation component and a solid acid-acting refractory support in a second zone;
- (3) separating the portion boiling in the lubricating oil boiling range from the effluent of the second zone;

- and
- (4) dewaxing this portion to recover a substantially wax-free lubricating oil or lubricating oil component.

- Preferably, the feedstock to the first zone is a wax obtained from a residual oil, and preferably the isomerizations in the first and second zones are carried out at temperatures in the range 316 to 492° C, pressures in the range 35 to 140 atm abs, space velocities in the range 0.1 to 5 volumes of wax per hour per unit volume of catalyst and mole ratios of hydrogen to wax in the range 5 to 50.

- BE-A-627517 and corresponding GB-A-1002857 disclose and claim a process for the conversion of waxy hydrocarbons to give an oil product having a higher isoparaffin content than feedstock comprising contacting the hydrocarbons at elevated temperature and in the presence of hydrogen with a catalyst comprising a platinum group metal, a halogenatable refractory inorganic oxide support and at least 1% wt. of fluorine, the catalysts having been prepared by contacting the support at elevated temperature with the vapour of a fluorine compound of general formula:-



- (where X is carbon or sulphur and Y is fluorine or hydrogen) under conditions which do not destroy the oxide structure or give free fluoride or volatile metal fluorine complexes to give said catalyst containing at least 1% wt. of fluorine. Preferably, the feedstock contains at least 50% by weight of waxy hydrocarbons. Preferably, the hydrocarbons are contacted at a temperature of from 500 to 1000° F (260 to 537.8° C) and a gauge pressure of from atmospheric to 3000 psig (0 to 20.685 MPa).

The present invention provides a process for producing lube oil base stocks or blending stocks having a pour point of -20°C or lower and a viscosity index of 130 and higher by the isomerization of wax, said process comprising the steps of (1) isomerizing the wax in an isomerization unit over an isomerization catalyst to a level of conversion such that from 15 to 35% unconverted wax, calculated as (unconverted wax)/(unconverted wax + dewaxed oil) X100, remains in the fraction of the isomerate boiling in the lube boiling range sent to the dewaxing unit, wherein the catalyst contains a hydrogenating metal (e.g., Group VI and/or Group VIII) component supported on a halogenated (e.g., fluorided) refractory metal oxide (e.g., alumina), and the isomerization conditions comprise a temperature in the range of from 270 to 400°C , a pressure of from 500 to 3000 psi (3.45 to 20.69 MPa) H_2 , a gas rate of 1000 to 10,000 SCF/b (178.1 to 1780.9 liter gas/liter oil), and a space velocity in the range 0.1 to 10 v/v/hr, fractionating the total product from the isomerization zone into a lube fraction boiling in the $330^{\circ}\text{C}+$ temperature range, (2) solvent dewaxing said fraction in a single solvent dewaxing step wherein the wax separation temperature is in the range of from -25 to -35°C , and (3) recovering a lube oil product having a VI of at least 130 and a pour point of -20°C or lower.

The wax separation temperature in the solvent dewaxing step may be in the range of from -25 to -30°C . The level of conversion may be from 20 to 30% unconverted wax.

The process may comprise recovering a lube oil product having a pour point of -21°C or lower in step (3).

The wax which is fed to the isomerization unit may be a slack wax which has been hydrotreated so as to contain about 1 to 5 ppm nitrogen, about 1 to 20 ppm sulfur and which has been deoiled to contain 0 to 35 wt% oil.

The isomerate from the isomerization zone may be fractionated into a lube oil fraction boiling in the 330°C - 600°C range, preferably 370°C - 580°C .

The solvent dewaxing step may be practised using C_3 - C_6 ketones, C_6 - C_{10} aromatic hydrocarbons, mixtures of C_3 - C_6 ketones and aromatic hydrocarbons, liquified, normally gaseous C_2 - C_4 hydrocarbons. The solvent dewaxing step may be practised using a mixture of methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) in a ratio of 20/80 at a temperature in the range -25 to -30°C . The solvent dewaxing step may be practised using methyl-isobutyl ketone.

Unconverted wax recovered in the dewaxing step and/or the fraction boiling above 600°C may be recycled to the further isomerized.

The novel process disclosed herein for the production of non-conventional lube oil base stocks or blending stocks of very low pour point, i.e., a pour point of -20°C or lower, e.g., -21°C or lower, preferably -24°C or lower, said pour points being achieved by conventional dewaxing techniques without resort to deep dewaxing procedures, and very high viscosity index (VI), VI's of 130, and higher, preferably 135 and higher by the isomerization of waxes over isomerization catalysts in an isomerization unit to a level of conversion such that 15-35%, preferably 20-30%, unconverted wax remains in the fraction of the isomerate boiling in the lube boiling range sent to the dewaxing unit calculated as (unconverted wax/unconverted wax + dewaxed oil)X100. For the purposes of this application the amount of unconverted wax in the $370^{\circ}\text{C}+$ oil fraction is taken to be the amount of wax removed or recovered from said oil fraction upon dewaxing. The total product from the isomerization (isom) unit is fractionated into a lube oil fraction boiling in the 330°C - 600°C range, preferably in the 370 - 580°C range. This lube oil fraction is solvent dewaxed preferably using 20/80 mixture of MEK/MIBK and unconverted wax is recycled to the isomerization unit.

Operating the isomerization unit at a level of conversion such that the oil fraction sent to the dewaxer contains 15 - 35% wax, preferably 20-30% unconverted wax goes against the conventional wisdom of isomerization operations. Lower levels of conversion, i.e. those levels at which a substantial portion of wax remains unconverted in the lube oil fraction sent to the dewaxer (and is subsequently recovered at the dewaxer for recycle) are typically seen as favoring maximization of lube oil production since operation at lower levels of conversion tend to favor the production of lube oil as compared to lower boiling fuels. The amount of wax present in the oil sent to the dewaxer normally should have no significant impact on the dewaxability of the oil or the pour point which can be achieved. There may be a point beyond which so much wax is present as to be beyond the ability of the dewaxer to handle the volume of waxy oil but this traditionally is a materials handling problem and does not affect the ability of the dewaxer to dewax oil to the desired pour point using conventional dewaxing techniques and temperatures. High levels of conversion however tend to produce larger quantities of fuels.

It has been discovered, that at low levels of conversion difficulty is encountered in producing a lube oil having a pour point of at least -21°C from wax isomerate. To produce a lube oil fraction which can be easily dewaxed to a pour point of at least -21°C it has been found that the isomerization unit should be run at a level of wax conversion such that 15-35%, preferably 20-30% unconverted wax is in the lube fraction

sent to the dewaxer.

Figure 1 is a schematic of the step sequences of the process of the present invention.

Figure 2 is a schematic of the step sequences of the process of the present invention including the optional step of waxy fractionator bottoms recycle.

Figure 3 illustrates the conversion behavior for three different Pt F/Al₂O₃ catalysts on a light slack wax (obtained from 600N raffinate) containing about 22% oil.

In Figure 3, the shape of the curves on the ternary diagram are a measure of the selectivity for converting wax into oil (e.g. 370°C oil) and fuels (e.g. product boiling below 370°C-). These curves were generated by running the catalysts on a 600N wax feed at conditions of 1000 psi H₂, 0.9 VV/hr, 5000 SCF/bbl, H₂, and temperatures ranging from 280-380°C.

The most selective catalysts produce higher oil yields and less fuel at any given residual wax level. Catalyst I (Catalyst 1 of Example 4 herein) produces a maximum once through oil yield of almost 55 wt.% on feed. Catalysts II (catalyst 8 of Example 5 herein) and III (comparison catalyst 1 of Example 5) produce maximum once-through oil yields of about 50 and about 45 wt.% respectively. Though the curves represent catalyst selectivity on a once through operation, they are a good guide to performance in a recycle-to-extinction process.

In principle a wax extinction process for maximizing lube yields would involve operation at a very low severity i.e. where conversion to fuels is at a minimum. Under these circumstances the amount of unconverted wax recycled to the isomerization reactor would be large and differences in catalyst selectivity would be less important.

In practice however, it is not possible to operate in a low conversion mode. Instead, the operating severity is governed by the need to make a low pour ($\leq -21^\circ\text{C}$ pour point) oil. It has been discovered that low pours cannot be achieved from isomerates made at low conversion. This is unexpected since with natural oils the amount of wax present did not affect the ability to dewax the oil to low target pour point. A critical determinant in reaching low pours is that the amount of wax remaining in the 370C+ fraction obtained from isomerization should not exceed 35% and for lower pour points may have to be as little as 25%. To maximize yield in this situation the choice of catalyst becomes important.

As wax in 370C+ oil product declines from 50 to 25%, (Figure 3), the ratio of oil to fuels decreases. This trend is much more pronounced with the least selective catalyst III. This is also illustrated in the Table below. All yields are based on a once through operation.

Catalyst	I			II			III		
	25	40	50	25	40	50	25	40	50
% Wax in oil product	18.5	34	44.5	17	32	43	12	30	42
Wax left (% of feed)	54.5	50	44.5	49.5	48	43	38	45	42
Oil yield (% of feed)	27.0	16	10	33.5	20	14	52	25	16

The full recycle oil yields for catalysts I, II and III, in which wax is recycled to extinction, can be predicted assuming the same conversion selectivity applies for recycled wax. On this basis, the yield distinctions between catalysts are even more pronounced.

Catalyst	-I-			-II-			-III-		
	25	40	50	25	40	50	25	40	50
% Wax in oil (once-through)	69	78	82	60	72	79	40	62	72
Predicted extinction recycle yield of 370C+ oil									

At a 25% wax in oil conversion level, Catalyst I is actually 70% more selective for oil than Catalyst III in an extinction recycle process. Thus small differences in catalyst selectivity identified in once through operations can translate into significant yield differences in a recycle process.

Another way to express the different performance of each catalyst is to determine the reaction severity required to achieve a particular target oil yield in a full recycle operation. For the target of 70% oil yield shown in Figure 3, catalyst I converts much more wax into oil than does catalyst III (i.e. there is less unconverted wax remaining in catalyst I product). In this case, catalyst III cannot simultaneously meet a target yield of 70% oil and a target of $\leq -21^\circ\text{C}$ pour point, since the amount of unreacted wax in oil exceeds 40%.

The wax which is isomerized may come from any of a number of sources. Synthetic waxes from Fischer-Tropsch processes may be used, as may be waxes recovered from the solvent or autorefri-
 5 dewaxing of conventional hydrocarbon oils as well as mixtures of these waxes. Waxes from dewaxing
 conventional hydrocarbon oils are commonly called slack waxes and usually contain an appreciable amount
 of oil. The oil content of these slack waxes can range anywhere from 0 to 45% or more, usually 5 to 30%
 oil. For the purposes of this application, the waxes are divided into two categories: (1) light paraffinic waxes
 boiling in the range about 300-580°C and (2) heavy micro waxes having a substantial fraction (>50%)
 boiling above 600°C.

Isomerization is conducted over a catalyst containing a hydrogenating metal component typically one
 10 from Group VI or Group VIII or mixtures thereof, preferably Group VIII, more preferably noble Group VIII
 most preferably platinum on a halogenated refractory metal oxide support. The catalyst typically contains
 from 0.1-5.0 wt.% metal, preferably 0.1 to 1.0 wt.% metal, most preferably 0.2-0.6 wt.% metal. The
 refractory metal oxide support is typically a transition e.g. gamma or eta alumina and the halogen is most
 usually fluorine.

A preferred catalyst contains a hydrogenation metal component which is a Group VIII metal or mixtures
 15 thereof, preferably noble Group VIII metal, most preferably platinum on a fluorided alumina or material
 containing alumina, preferably alumina or material consisting predominantly (i.e. >50%) of alumina, most
 preferably gamma or eta alumina wherein said catalyst in its as introduced to waxy feed form is
 characterized by possessing (1) a hydrate level of 60 or less, preferably 10 to 60 determined as the relative
 20 amount of hydrate represented by a peak in the X-ray diffraction (XRD) pattern at $2\theta = 5.86^\circ$ when a
 hydrate level of 100 corresponds to the XRD peak height exhibited by a standard material constituting 0.6
 wt% Pt on 150 m²/g γ alumina containing 7.2 wt% F wherein the fluorine has been deposited using an
 aqueous solution containing a high concentration of HF, i.e. 10 wt% HF and greater, preferably 10 to 15
 25 wt% HF and the material dried at 150°C for 16 hrs; (2) a surface nitrogen content N/AI ratio of 0.01 or less,
 preferably 0.007 or less, most preferably 0.004 or less as determined by X-ray photoelectron spectroscopy
 (XPS); (3) a bulk fluorine concentration of about 2 to 10 wt% and (4) a surface fluorine present in a layer
 extending from the surface of the particle (e.g. 1/16 inch extrudates) to a depth of 1/100 inch, of less than 3
 wt%, preferably less than 1 wt%, most preferably less than 0.5 wt% fluorine in that zone provided that the
 surface fluoride concentration is less than the bulk fluoride concentration.

The fluoride content of the catalyst can be determined in a number of ways.

One technique analyzes the fluorided catalyst using oxygen combustion methodology which is well
 30 established in the literature. Approximately 8-10 mgs of sample is mixed with 0.1 g benzoic acid and 1.2
 gms of mineral oil in a stainless steel combustion capsule which is mounted in a 300 mL Parr oxygen
 combustion bomb. The "sample" is purged of air and subsequently combusted under 30 Atms of pure
 35 oxygen. Combustion products are collected in 5 mL of deionized water. Once the reaction has gone to
 completion (about 15 minutes), the absorbing solution is quantitatively transferred and made to fixed
 volume.

Fluoride concentration of the sample is determined by ion chromatography analysis of the combustion
 product solution. Calibration curves are prepared by combusting several concentrations of ethanolic KF
 40 standards (in the same manner as the sample) to obtain a 0-10 ppm calibration range. Fluoride concentra-
 tion of the catalyst is calculated on an ignition-loss-free-basis by comparison of the sample solution
 response to that of the calibration curve. Ignition loss is determined on a separate sample heated at 800
 degrees F for at least 2 hours. Ion chromatographic analysis uses standard anion conditions.

Another procedure employs the use of fluoride distillation with a titrimetric finish. Fluorides are
 45 converted into fluorosilicic acid (H_2SiF_6) by reaction with quartz in phosphoric acid medium, and distilled as
 such using super heated steam. This is the Willard-Winter-Tananaev distillation. It should be noted that the
 use of super heated, dry (rather than wet) steam is crucial in obtaining accurate results. Using a wet steam
 generator yielded results 10-20% lower. The collected fluorosilicic acid is titrated with standardized sodium
 hydroxide solution. A correction has to be made for the phosphoric acid which is also transferred by the
 50 steam. Fluoride data are reported on an ignition-loss-free-basis after determination of ignition loss on a
 sample heated to 400 degree C for 1 hour.

Another preferred catalyst is a catalyst prepared by a process involving depositing a hydrogenation metal
 on an alumina or material containing alumina support, calcining said metal loaded support typically at
 between 350 to 500°C, preferably about 450 to 500°C for about 1 to 5 hrs, preferably about 1 to 3 hrs and
 55 fluoriding said metal loaded support using a high pH fluorine source solution to a bulk fluorine level of about
 8 wt% or less (e.g., 2 to 8 wt%), preferably about 7 wt% or less, said high pH source solution being at a pH
 of 3.5 to 4.5 and preferably being a mixture of NH_4F and HF followed by rapid drying/heating in a thin bed
 or rotary kiln to insure thorough even heating in air, oxygen containing atmosphere or an inert atmosphere

to a temperature between about 350 to 450°C in about 3 hours or less, preferably 375 to 400°C and holding at the final temperature, if necessary, for a time sufficient to reduce the hydrate and nitrogen content to the aforesaid levels, e.g. holding for 1 to 5 hours or using a low pH fluorine source solution having a pH or less than 3.5 to a bulk fluorine level of about 10 wt% or less (e.g., 2 to 10 wt%), preferably about 8 wt% or less followed by drying/heating in a thin bed or rotary kiln to a temperature of about 350 to 450°C, preferably 375 to 425°C and holding, if desired, at that temperature for 1 to 5 hours, in air, an oxygen containing atmosphere, or inert atmosphere. The alumina or alumina containing support material is preferably in the form of extrudates and are preferably at least about 1/32 inch across the longest cross sectional dimension. If the catalyst is first charged to a unit, heating a dense bed charge of catalyst will be for a longer period, longer than 5 hours, preferably longer than 10 hours and preferably at temperatures of 400 to 450°C.

The above catalysts typically contain from 0.1 to 5.0 wt% metal, preferably 0.1 to 1.0 wt% metal, most preferably 0.2 to 0.6 wt% metal.

The dried/heated catalyst has a surface nitrogen content N/AI of 0.01 or less by X-ray photo-electron spectroscopy (XPS), preferably an N/AI of 0.007 or less, most preferably an N/AI of 0.004 or less by XPS.

The catalyst, following the above recited heating step, can be charged to the isomerization reactor and brought quickly up to operating conditions. Alternatively following the above recited heating step the catalyst prepared using the pH 3.5 - 4.5 solution technique can be activated preferably in pure or plant hydrogen (60-70 vol% H₂) at 350 to 450°C, care being taken to employ short activation times, from 1 to 24 hours, preferably 2 to 10 hours being sufficient. Long activation times (in excess of 24 hours) have been found to be detrimental to catalyst performance. By way of comparison, catalysts made using solutions of pH less than 3.5 can be activated in pure or plant hydrogen at 350 to 500°C for from 1 to 48 hours or longer. In fact, if catalysts prepared using solutions of pH 3.5 or less are not heated first, then it is preferred that they be subsequently activated at more severe conditions, i.e. for longer times and/or at higher temperatures. On the other hand, if they are heated first, then moderate activation procedures similar to those employed with catalysts made from the higher pH solution treatment will suffice.

A typical activation profile shows a period of 2 hours to go from room temperature to 100°C with the catalyst being held at 100°C for 0 to 2 hours then the temperature is raised from 100 to about 350 over a period of 1 to 3 hours with a hold at the final temperature of from 1-4 hours. Alternatively the catalyst can be activated by heating from room temperature to the final temperature of 350-450°C over a period of 2-7 hours with a hold at the final temperature of 0-4 hours. Similarly activation can be accomplished by going from room temperature to the final temperature of 350-450°C in 1 hour.

It is possible to dispense with a separate activation procedure entirely, (provided the catalyst has first been heated in air). In these instances, the calcined catalyst is simply charged to the reactor, heated to just above the melting point of the wax feed, feed and hydrogen introduced onto the catalyst, and thereafter the unit brought quickly up to operation conditions.

Another preferred catalyst comprises a hydrogenating metal on fluorided alumina or material containing alumina support made by depositing the hydrogenation metal on the support and fluoriding said metal loaded support using acidic fluorine sources such as HF by any convenient technique such as spraying, soaking, incipient wetness, etc. to deposit between 2-10%F preferably 2-8%F. Following halogenation the catalyst is dried, typically at 120°C and then crushed to expose inner surfaces, the crushed catalyst and is double sized to remove fines and uncrushed particles. This sieved catalyst is 1/32 inch and less and typically from 1/64 to 1/32 inch in size across its largest cross-sectional dimension.

The starting particle or extrudate may be of any physical configuration. Thus particles such as cylinders, trilobes or quadri lobes may be used. Extrudates of any diameter may be utilized and can be anywhere from 1/32 of an inch to many inches in length, the length dimension being set solely by handling considerations. It is preferred that following sizing the particle have a length smaller than the initial extrudate diameter.

Following deposition of the hydrogenation metal and the fluoriding of the particle or extrudate, the particle or extrudate is crushed or fractured to expose inner surfaces.

The crushing is conducted to an extent appropriate to the particle or extrudate with which one is starting. Thus, an extrudate which is 1 foot long and 1/16 inch in diameter would be sized into pieces which range anywhere from 1/64 to 1/32 inch across its longest cross-sectional dimension. Similarly, if the extrudate is only 1/16 inch to begin with it will be enough simply to break it in half, into two 1/32 inch pieces, for example.

Alternatively, one can take a metal loaded support particle which is already about 1/32 inch in size or smaller and fluoride it as described above using HF.

Generally, therefore, the sized material will range in size between about 1/64 to 1/32 inch in size.

The uncalcined sized catalyst is activated in a hydrogen atmosphere such as pure hydrogen or plant hydrogen containing 60 to 70 vol% hydrogen by heating to 350 to 500° C, preferably 350 to 450° C for from 1 to 48 hours or longer. The hydrogen activation profiles described above may similarly be employed here.

This sized catalyst is unexpectedly superior for wax isomerization as compared to the uncrushed particle or extrudate starting material. It has also been discovered that 370° C⁺ oil products made using the sized catalyst as compared to the uncrushed or extrudate material starting with wax possessing about 5-10% oil exhibit higher VI's than do 370° C⁺ oil products made starting with wax possessing 0% oil (on the one hand) and about 20% oil (on the other). Therefore, to produce products having the highest VI one would isomerize wax having from 5-15% oil, preferably 7-10% oil using the "sized" catalyst produced using HF.

As one would expect isomerization catalysts are susceptible to deactivation by the presence of heteroatom compounds (i.e. N or S compounds) in the wax feed so care must be exercised to remove such heteroatom materials from the wax feed charges. When dealing with high purity waxes such as synthetic Fischer-Tropsch waxes such precautions may not be necessary. In such cases subjecting such waxes to very mild hydrotreating may be sufficient to insure protection for the isomerization catalyst. On the other hand waxes obtained from natural petroleum sources contain quantities of heteroatom compounds as well as appreciable quantities of oil which contain heteroatom compounds. In such instances the slack waxes should be hydrotreated to reduce the level of heteroatoms compounds to levels commonly accepted in the industry as tolerable for feeds to be exposed to isomerization catalysts. Such levels will typically be a N content of about 1 to 5 ppm and a sulfur content of about 1 to 20 ppm, preferably 2 ppm or less nitrogen and 5 ppm or less sulfur. Similarly such slack waxes should be deoiled prior to hydrotreating to an oil content in the range of 0-35% oil, preferably 5-25% oil. The hydrotreating step will employ typical hydrotreating catalyst such as Co/Mo, Ni/Mo, or Ni/Co/Mo on alumina under standard, commercially accepted conditions, e.g., temperature of 280 to 400° C, space velocity of 0.1 to 2.0 VV/hr, pressure of from 500 to 3000 psig H₂ and hydrogen gas rates of from 500 to 5000 SCF/b.

In the present invention isomerization of waxes over the above particularly recited isomerization catalysts is conducted to a level of conversion which optimizes the conversion of wax to lube range materials while minimizing production of fuels range materials (i.e. 370° C⁻ products) yet producing an overall lube oil product which does not contain more unconverted wax than can be efficiently handled by the solvent dewaxing unit i.e. 25-35% wax to the dewaxer.

Isomerization is conducted under conditions of temperatures between 270 to 400° C, preferably 300-360° C, pressures of 500 to 3000 psi H₂, preferably 1000-1500 psi H₂, hydrogen gas rates of 1000 to 10,000 SCF/bbl, and a space velocity in the range 0.1-10 v/v/hr, preferably 1-2 v/v/hr.

Following isomerization the isomerate is fractionated into a lubes cut and fuels cut, the lubes cut being identified as that fraction boiling in the 330° C⁺ range, preferably the 370° C⁺ range or even higher. This lubes fraction is then dewaxed to a pour point of about -21° C or lower. Dewaxing is accomplished by techniques which permit the recovery of unconverted wax, since in the process of the present invention this unconverted wax is recycled to the isomerization unit. It is preferred that this recycle wax be recycled to the main wax reservoir and be passed through the hydrotreating unit to remove any quantities of entrained dewaxing solvent which solvent could be detrimental to the isomerization catalyst. Alternatively, a separate stripper can be used to remove entrained dewaxing solvent or other contaminants. Since the unconverted wax is to be recycled dewaxing procedures which destroy the wax such as catalytic dewaxing are not recommended. Solvent dewaxing is utilized and employs typical dewaxing solvents. Solvent dewaxing utilizes typical dewaxing solvents such as C₃-C₆ ketones (e.g. methyl ethyl ketone, methyl isobutyl ketone and mixtures thereof), C₆-C₁₀ aromatic hydrocarbons (e.g. toluene) mixtures of ketones and aromatics (e.g. MEK/toluene), autorefrigerative solvents such as liquified, normally gaseous C₂-C₄ hydrocarbons such as propane, propylene, butane, butylene and mixtures thereof, etc. at filter temperature of -25 to -30° C. The preferred solvent to dewax the isomerate especially isomerates derived from the heavier waxes (e.g. bright stock waxes) under miscible conditions and thereby produce the highest yield of dewaxed oil at a high filter rate is a mixture of MEK/MIBK (20/80 v/v) used at a temperature in the range -25 to -30° C. Pour points lower than -21° C can be achieved using lower filter temperatures and other ratios of said solvents but a penalty is paid because the solvent-feed systems becomes immiscible, causing lower dewaxed oil yields and lower filter rates. Further, when dewaxing isomerate made from a microwax, e.g. Bright Stock slack wax it is preferred that the fraction of the isomerate which is sent to the dewaxer is the "broad heart cut" identified as the fraction boiling between about 330 to 600° C, preferably about 370-580° C. After such fractionation the fraction sent to the dewaxer has about 35% or less unconverted wax. The heavy bottoms fraction boiling above about 580 to 600° C contains appreciable wax and can be recycled to the isomerization unit directly. However if any hydrotreating or deoiling is deemed necessary or desirable then

the fractionation bottoms are reisolomerized by being first sent to the fresh feed reservoir and combined with the wax therein.

It has also been found that prior to fractionation of the isomerate into various cuts and dewaxing said cuts the total liquid product (TLP) from the isomerization unit can be advantageously treated in a second stage at mild conditions using the isomerization catalyst or simply noble Group VIII on refractory metal oxide catalyst to reduce PNA and other contaminants in the isomerate and thus yield an oil of improved daylight stability.

In that embodiment the total isomerate is passed over a charge of the isomerization catalyst or over just noble Gp VIII on e.g. transition alumina. Mild conditions are used, e.g. a temperature in the range of 170-270°C, preferably 180 to 220°C, at pressures of 300 to 1500 psi H₂, preferably 500 to 1000 psi H₂, a hydrogen gas rate in the range of from about 500 to 10,000 SCF/bbl and a flow velocity of about 0.25 to 10 v/v/hr., preferably about 1-4 v/v/hr. Temperatures at the high end of the range should be employed only when similarly employing pressures at the high end of their recited range. Temperatures in excess of those recited may be employed if pressures in excess of 1500 psi are used, but such high pressures may not be practical or economic.

The total isomerate can be treated under these mild conditions in a separate, dedicated unit or the TLP from the isomerization reactor can be stored in tankage and subsequently passed through the aforementioned isomerization reactor under said mild conditions. It has been found to be unnecessary to fractionate the 1st stage product prior to this mild 2nd stage treatment. Subjecting the whole product to this mild second stage treatment produces an oil product which upon subsequent fractionation and dewaxing yields a base oil exhibiting a high level of daylight stability and oxidation stability. These base oils can be subjected to subsequent hydrofinishing using conventional catalysts such as KF-840 or HDN-30 (e.g. Co/Mo or Ni/Mo on alumina) at conventional conditions to remove undesirable process impurities to further improve product quality.

Figures 1 and 2 present schematic representations of preferred embodiments of the wax isomerization process.

In Figure 1, slack wax feed, derived from, for example a lighter oil such as 600N oil or lighter is fed from reservoir (1) to a hydrotreater (3) via line 2 wherein heteroatom compounds are removed from the wax. This hydrotreated slack wax is then fed via line 4 to the isomerization unit (5) after which the total liquid product is fed either directly via lines 6, 6B and 6D to the separation tower (unit 8) for fractionation into a lube fraction boiling above 370°C* and a light fraction boiling below 370°C* or, in the alternative the TLP from the isomerization unit is fed first via lines 6 and 6A to a low temperature, mild condition second stage treating unit (unit 7) wherein the TLP is contacted with the isomerization catalyst or simply a noble Group VIII metal on alumina catalyst to produce a stream which is then sent via lines 6C and 6D to the fractionation tower (unit 8). In either case the lube steam boiling in the 370°C* range is then forwarded via line 9 to the solvent dewaxer (unit 10) for the separation of waxy constituents therefrom, the dewaxed oil fraction being recovered via line-11 and if necessary forwarded to other conventional treatment processes normally employed on base stock or blending stock oils. The recovered wax is recycled either directly via line 12 and 12A to the slack wax stream being fed to the isomerization unit or it is recycled to the wax reservoir (1) via line 12B for passage through the hydrotreater prior to being recycled to the isomerization unit.

In Figure 2 the wax processing stream is much like that of Figure 1, the main differences being that Figure 2 represents the scheme for handling heavier slack wax feeds, such as a wax feed derived from Bright Stock oil. In such a case the wax from reservoir 1 is fed via line 2 to the hydrotreater (3) prior to being sent via line 4 to the isomerization unit (unit 5) after which it is either fed via lines 6 and 6A to a low temperature mild condition second stage treating unit (unit 7) wherein it is contacted with a further charge of isomerization catalyst or simply noble Group VIII metal on alumina and fed via lines 6C and 6D to the fractionator tower (unit 8), or fed directly via lines 6, 6B and 6D to the fractionation tower (unit 8). In the fractionation tower the isomerate made using the heavy wax is fractionated into a light fraction boiling in the 370°C* (a fuels cut) a lube cut boiling in the 370°C* range and a bottoms fraction boiling in the 580°C* range. The lube fraction, a broad cut boiling in the 370°C* to 580°C* range is sent via line 9 to the dewaxer (unit 10) as previously described. The 580°C* bottoms fraction contains appreciable wax and is recycled via line 13, 13A, 13B and 4 to the isomerization unit (5). This bottoms fraction optionally can be combined via line 13 and 13C with the wax in line 12 recovered from the dewaxing unit (10) in which case this total recycled stream can be fed directly to the isomerization unit via lines 12A, 13B and 4 or it can be sent to the wax reservoir (1) via lines 12B for treatment in the hydrotreater prior to being fed to the isomerization unit.

The invention will be better understood by reference to the following examples which either demonstrate the invention or are offered for comparison purposes.

EXAMPLES

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Example 1

Catalyst 1

10 A synthetic hydrocarbon synthesis wax (a Fischer-Tropsch wax), characterized as being 100% 370°C + material possessing a melting point in the range 104 to 110°C, a mean carbon number (from viscosity data) of about 65 carbons, a boiling range of about 450-650°C (initial to 70 LV% off by GCD) and a kinematic viscosity of 9.69, was isomerized over a 14/35 meshed platinum on fluorided alumina catalyst made by first
 15 fluoriding a platinum loaded 1/16" alumina extrudate (0.6 wt.% platinum) using a 11.8 wt% aqueous HF solution (by soaking) after which the fluorided metal loaded extrudate was washed with 10 fold excess water and dried at 150°C in vac. oven. The metal loaded fluorided extrudate was not calcined. It was crushed to produce particles of about 1/30" (meshed to 14/35). Catalyst 1 had a fluorine content of 8.3 wt%.

The sized catalyst, Catalyst 1, was activated by heating to 450°C in 50 psi flowing H₂ in the following
 20 manner: room temperature to 100°C in 2 hours, hold at 100°C for 1 hour; heat from 100°C to 450°C in 3 hours, hold at 450°C for 1 hour.

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Table 1
DENAXING FISCHER-TROPSCH SYNTHETIC WAX HYDROISOMERATES (370°C+)

Isomerization, Conditions	1000	1000	1000
Pressure, psi H ₂	1.0	1.0	1.0
space velocity (v/v/hr)	7500	7500	7500
gas treat rate (SCF/bbl, H ₂)	375-378	380.5	380.5
Temp., °C	4082-4584	4981-5287	4981-5287
Time on stream (hrs)	(LOW)	(HIGH)	(HIGH)
Conversion Level	13	19	19
Wt% 370°C-	98	86	86
Waxy Product Properties			
Cloud °C			
Dewaxing Conditions			
Solvent:			
Dilution:			
Filter temperature, °C			
Viscosity, cst @100°C			
Dewaxed Oil Properties			
Pour, °C			
Pour-Filter DT, °C			
Viscosity, cst @40°C			
Viscosity, cst @100°C			
Viscosity Index			
Wt% Wax Recovered from 370°C+ Oil			

It is apparent that at low levels of conversion, where large quantities of unconverted wax remain in the 370°C+ oil to the dewaxer, it is not possible to achieve a low pour (i.e. about -21°C) using typical dewaxing solvents under standard conditions (i.e. filter temperature of -30°C). Lower pour point could be achieved if one were to go to extremely low filter temperature such as -40°C, but this puts strains on the refrigeration capability of the plant as well as possibly being beyond the metallurgical limitations of most plants. Operating at higher levels of conversion (e.g. 30% wax in the 370°C+ fraction to the dewaxer) is seen to facilitate achieving a low pour point while still being within the typical operating parameters of standard dewaxing plants.

Example 2

Catalyst 1

Slack wax from 600N oil was isomerized over Catalyst 1 described in Example 1 to three levels of conversion.

The slack wax was first hydrotreated over HDN-30 catalyst (a conventional Ni/Mo on alumina catalyst) at 350°C, 1.0 v/v/hr., 1500 SCF/BBL, H₂, 1000 psi (H₂). The catalyst had been on stream for 1447-1577 hours.

The hydrotreated slack wax had sulfur and nitrogen contents of less than 1 ppm and contained about 23% oil.

TABLE 2

DEWAXING OF ISOMERATES DERIVED FROM 600N SLACK WAX (370° C +)				
Isomerization Conditions		1000	1000	1000
Pressure, psi		0.9	0.9	0.9
Space Velocity (v/v/hr)		5000	5000	5000
Gas treat rate (SCF/bbl, H ₂)		318	324	327
Temp. °C		(Low)	(Medium)	(High)
Conversion Level		11.8	20	25.8
Wt%370° C- Dewaxer Feed Cloud, °C		60	54	49
Dewaxing Conditions (Batch Conditions)		100% MIBK		
Solvent:		5.1	3.5	3.4
Dilution Solvent/Feed v/v		-25	-25	-25
Filter Temperature, °C		5.63	5.03	4.61
Viscosity, cS @ 100° C				
Dewaxed Oil Properties		-14	-19	-23
Pour Point, °C		11	6	2
Pour-Filter T °C		27.8	22.8	20.7
Viscosity, cST @ 40° C		5.63	5.03	4.61
Viscosity, cST @ 100° C		149	147	144
Viscosity Index		56	39	30
Wt.% Wax recovered from 370° C + oil fraction				

From this it is seen that even for isomerates obtained by isomerizing waxes from a natural petroleum source, the ability to dewax the isomerate to the desired low pour point of at least about -21° C is dependent upon the level of conversion. Low conversion levels produce isomerate which cannot be dewaxed to a low target pour using conventional dewaxing solvents under typical dewaxing filter temperature conditions.

EXAMPLE 3 (Comparative)

It has been discovered that waxy isomerates behave differently than waxy conventional oils when being dewaxed. With waxy conventional oils the wax content of the oil (usually a solvent extracted distillate) has virtually no impact on the pour point of the dewaxed oil nor on the ease with which that pour point can be achieved. In Table 3 below two typical oils, 150 neutrals having viscosities of about 5.4 cSt @100° C, viscosities very similar to those of the isomerates described in the present text, were solvent dewaxed using ketone solvents. The difference between the two natural oil stocks is wax content; one stock from a South Louisiana crude contains about 9-10% wax, the other stock from a North Louisiana crude contains about 19-22% wax. Both stocks were processed under nearly identical conditions as shown in the Table. Despite the differences in wax content the pour points of the dewaxed oils obtained by dewaxing under nearly identical conditions were identical. Both natural oil stocks were dewaxed in a dewaxing plant employing MEK/MIBK under DILCHILL conditions as described in U.S. Patent 3,773,850 to a temperature of -8° C. Further chilling to the filtration temperature was done employing laboratory scraped surface chilling apparatus. While feed filter rates and wax cake liquids/solids differed, both oils could be dewaxed to about the same pour point using nearly identical dewaxing conditions.

This is to be compared with the results obtained in the prior example wherein dewaxing isomerate of different wax contents under nearly identical dewaxing conditions gave dewaxed oils of different pour points, thus showing the unexpected effect that the wax content of the isomerate has on dewaxing performance.

Table 3

Preparation of Conventional Stocks
 150 Neutral - 5.4 cSt @ 100°C Tube Fraction

Feed Crude Source	NMD V(11)	Filtration Temp °C	Prepared Feed Wt % Content %	Pour Point °C	Cloud Point °C	Feed Filter Rate m ³ /m ² /d	Max Cake L/S v/v	Dilution Ratio v/v	MEK/MIBK v/v
South L.A.	90	-20	9-10	-18	28	6.6	8.8	2.5	40/60
North L.A.	105	-21	19-22	-18	11	11.0	4.6	2.8	40/60

(1) Both stocks extracted using N-methyl pyrrolidone to the maximum possible viscosity index.

(2) Solvent composition required for miscible filtration at the filtration temperatures shown are typically MEK/MIBK, 60/40 for both stocks.

EXAMPLE 4

Catalysts 2 to 7

5 In the following runs the isomerate was made from slack wax obtained by solvent dewaxing a 600N oil. The slack wax was hydrotreated over HDN-30 catalyst at 350°C, 1.0 v/v/hr. 1500 SCF/bbl, H₂, 1000 psi H₂ or over KF-840 at 340°C, 0.5 v/v/hr., 1000 psi, 1500 SCF/bbl. These hydrotreated waxes had oil contents ranging from 21 to 23%, S ranging from 3 to 10 (ppm), N ≤1 (ppm).

This wax feed was contacted with platinum on fluorided alumina produced in the following way.
 10 Catalyst 2 One sixteenth inch γ alumina extrudates impregnated with platinum were obtained from the commercial supplier containing 0.6 wt.% platinum and 1% chlorine on the extrudate. The metal loaded extrudate was then fluorided using a 10 fold excess 11.6 wt% aqueous HF by immersion for 16 hrs. at ambient temperature. The resulting catalyst was washed with 2 fold excess H₂O and dried at 150°C in vacuum for 16 hrs. The fluoride content was 8.0 wt.%. The sample of Catalyst 2 as charged to the 200 cc
 15 unit was activated in 300 psi H₂ at 6.3 SCF H₂/hr as follows: heat from room temperature to 100°C at 35°C/hr; hold at 100°C for 6 hrs; heat from 100°C to 250°C at 10°C/hr; hold at 250°C for 12 hrs; heat to 400°C at 10°C/hr; hold at 400°C for 3 hrs. The sample of Catalyst 2 as charged to the 3600 cc unit was activated as follows: at 300 psi H₂ at 11 SCF H₂/hour per pound of catalyst, heat from room temperature to 100°C at 10°C/hour; hold at 100°C for 24 hours; heat from 100°C to 250°C at 10°C per hour; hold at
 20 250°C for 15 hours; then at 22 SCF H₂/hour per pound of catalyst, heat from 250 to 400°C in 31 hours; hold at 400°C for 3 hours.

Catalyst 3 was prepared using 1/16 inch γ alumina extrudates impregnated with 0.6 wt% platinum and containing 1.0% chlorine as received from the commercial supplier. The metal loaded extrudate was then fluorided using 5:1 volume excess of 11.6 wt% aqueous HF by immersion for 6 hours at ambient
 25 temperature (~ 25°C). The resulting material when washed with two-fold excess H₂O and dried at about 120°C for 16 hrs as designated Catalyst 3. The bulk fluorine content was 7.2 wt%. Catalyst 3 was activated in atmospheric pressure H₂ by heating from room temperature to 343°C in 4 hours followed by a hold at 343°C for 2 hours.

Catalyst 4 is the same as catalyst 3 in all respects except that prior to the hydrogen activation step the material was heated at 400°C in air for 3 hours.

30 Catalyst 5 One sixteenth inch alumina extrudates impregnated with platinum were obtained from a commercial supplier containing 0.6 wt.% platinum and 1% chlorine. The metal loaded extrudate was fluorided using a solution of NH₄F/HF at pH 4.2 by soaking. The soaked material was washed, then dried/heated for 2 hours at 400°C in air. Fluorine content was found to be 7.0 wt%, and the surface N/Al =
 35 .0037 by X-ray photo spectroscopy. Catalyst 5 was activated by heating in 50 psi flowing H₂ as follows: room temperature to 100°C in 2 hrs., hold for 1 hr., 100°C to 450°C in 3 hrs., hold for 4 hrs. For the sample of catalyst 5 charged to the small unit (b) used in the reported Table 4, the final activation condition was 400°C for 0.75 hours.

Catalyst 6 was prepared by meshing the dried/heated form of Catalyst 5 to a particle size of 1/30" (14/35 mesh). After meshing to a particle size of 1/30" (14/35 mesh), Catalyst 6 was activated in flowing hydrogen
 40 by heating from room temperature to 100°C over a 2 hour period, holding at 100°C for 1 hour, heating from 100 to 450°C over a 3 hour period, holding at 450°C for 1 hour. Activation pressure was 50 PSI. Catalyst 7 1/16" Al₂O₃ extrudates were impregnated with chloroplatinic acid to a level of 0.26% pt. The extrudates were then sized and screened to 1/30" mesh and subsequently fluorided using a 10 fold excess
 45 of 11.6 wt% aqueous HF by immersion for 4 hrs at ambient temp. The resulting catalyst was washed in a 30 fold excess of H₂O and dried at 130°C for 16 hrs. The catalyst was not calcined. The fluorine content was found to be 8.5 wt%. Activation procedure was the same as employed for Catalyst 1 (See Example 1).

Table 4 presents comparisons of these catalysts on slack wax from 600N oil. Conditions are recited under which the catalysts were run. Dewaxed oil yields were determined by using the test method ASTM D-
 50 3235 on the 370°C⁺ fraction.

This example demonstrates that Catalyst 1 is unexpectedly superior to the extrudate form of the HF treated catalyst (Catalyst 2), even when Catalyst 2 is run at high mass velocity.

The importance of using the low pH halogenation media is also demonstrated, compare Catalyst 4 with Catalyst 6, when each was run in a small unit in the down flow mode, clearly, sizing down the particles does
 55 not always improve selectivity; it is only an advantage if fluoriding was originally performed at low pH (e.g. <4) using for example HF. The performance of Catalyst 7 of Table 4 also illustrates that the catalyst can be sized before fluoriding. Good selectivity again results when the low pH fluoriding media is used.

Table 4 also demonstrates the importance of the catalyst having a hydrate level of 60 or less. Catalyst 3 possesses a hydrate level of about 66 and is seen to be inferior to catalyst 4 which is identical except that the hydrate level is lower (57). Catalyst 4 produces a higher yield of 370° C. oil than does Catalyst 3.

TABLE 4										
Catalyst Unit	1 (a)	1 (b)	2 (a)	2 (a)	1 (a)	4 (a)	5 (a)	5 (b)	6 (b)	7 (b)
Cat Charge (cc)	200	80	3600	200	50	50	200	80	80	80
Flow	Up	Down	Down	Up	Up	Up	Up	Up	Down	Down
Catalyst Inspections										
N/AI by KPS					0.0012	0.0013				
Hydrate level					100	60				
N/AI level					0.0011	0.0013				
(after activation)					66	57				
Hydrate level										
(after activation)										
Isomerization Conditions										
Temp °C	347	320	323	318	313	315	340	320	310	320
Pressure (psi H ₂)	1000	1000	1000	1000	1000	995	1000	1000	1000	1000
LHSV (v/v/h)	0.9	0.9	1.0	1.0	0.45	0.45	0.9	0.9	0.9	0.9
Gas rate										
(SCF/bbl, H ₂)	5000	5000	5000	5000	5000	5000	5000	5000	5000	5000
Devised 370°C+ Oil Yield										
(Wt.% on feed)	56.0	52.0	51.0	45.0	47.1	51.7	50.0	48.0	39.0	51
370°C- Conversion	29.0	22.0	29.0	29.0	36.1	18.7	23.8	20.7	37.3	28.7
(wt.% on feed)										

* (a) = continuous pilot unit.
(b) = small lab unit.

* (a) - continuous pilot unit
(b) - small lab unit.

Example 5Catalysts 8 and 9 and Comparison Catalysts 1,2,3 and 4

6 In these Examples the hydrotreated 600N slack waxes are those previously described in Example 4. Following isomerization in an upflow once through mode of operation the isomerate was fractionated to obtain the 370 ° C⁺ lube fraction.

Dewaxed oil yields were determined using the ASTM Test D-3235 method on the 370 ° C⁺ fraction.

10 In this Example a series of catalysts was prepared using the NH₄F/HF fluoriding procedures described above. Examples of superior catalysts made using the NH₄F/HF fluoriding procedures were seen to have surface fluorine content in the low recited desirable range. Results for these catalysts are shown in Table 5. Less satisfactory catalysts made using NH₄F/HF treatment are shown in Table 6. These catalysts all contained high levels of surface fluorine resulting from initial excessive loading of bulk fluorine when using ph 4 or greater. In the case of comparison Catalyst 3, while the bulk fluorine level is within the desired
15 range and surface fluorine was initially low in the as charged catalyst, the excessively severe activation conditions employed subsequently increased the surface fluorine level of the catalyst. This we believe is the reason for its poorer selectivity. All catalysts were dried and heated as reported in Tables 5 and 6.

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Table 5

Examples of Good Catalysts in the Process of the Invention			
Catalyst	8	9	9
Catalyst Charge (cc) Method of fluoride treat Drying conditions °C	50 NH ₄ F/HF 400 (muffle)	50 NH ₄ F/HF 400	200 NH ₄ F/HF 400 rotary kiln
Catalyst Inspections	0.0037	0.0021	0.0021
N/AI by XPS	29	24	24
Hydrate level	6.9	7.0	7.0
F. (wt%) (bulk)	1.7	2.0	2.0
F wt% (surface)			
Hydrogen Activation Times, hrs.	7	4	7
Rt. to final temp	2	2	2
Time at T	343	343	350
Final T, °C			
Hydrogen Activation Pressure	ambient	ambient	50 psi
Isomerization Conditions			
Temp. °C	310	312	309
LHSV (v/v/h)	0.45	0.45	1.0
Press. PSI H ₂	1000	1000	1000
Gas rate (SCF/B, H ₂)	5000	5000	5000
Max 370 °C oil Dewaxed oil yield, (wt% on feed)	50(1)	49.8	49.3
Conversion to 370 °C (wt% on feed)	28	24.5	35.2

(1) Interpolated data

Table 6
Performance of Comparative Catalysts

Catalyst Unit Type Method Treat drying conditions, °C	Performance of Comparative Catalysts			
	Comparison 1	Comparison 2	Comparison 3	Comparison 4
Catalyst Unit Type Method Treat drying conditions, °C	NH ₄ F/HF 400 (rotary kiln) 0.010 6.8 ~10 19	Continuous Pilot Unit NH ₄ F/HF 400 (muffle) 0.013 5.6 ~5 <10	NH ₄ F/HF 400 (rotary kiln) 0.0021 7.0 • 24	NH ₄ F/HF 400 (muffle) 0.0040 6.9 7 <10
N/Al by XPS F, wt% (surface) Hydrate level				
Hydrogen Activation Times, hr.	2.1 2 1 350 50	2.1 2 1 350 50	1.6 42 1 400 300	2.1 2 1 350 50
RT to 100°C, 4100°C to final temp (°F)				
Time at T				
Final POC				
Hydrogen Activation pressure#				
Isomerization Conditions				
Temp, °C	310 0.90 1000 5000	300 0.90 1000 5000	305 1.0 1000 5000	310 0.90 1000 5000
LHSV (v/v/hr)				
Pressure psi H ₂				
Gas rate				
(SCR H ₂ /bbl)				
Devised Oil	44.0	45.0	45	48.5
Yield, (wt% on feed)	26.1	24.1	21.8	30.1
370°F				
(wt% on feed)				
Unconverted Wax	29.9	30.9	33.2	21.4
(wt% on feed)				

* P. at surface measured 2.0 before activation and approximately 7 after activation

EXAMPLE 6

50 The presence of oil in the wax has been found to produce an enhanced VI product as compared to oil free wax when isomerization is performed utilizing the preferred "sized" catalyst made employing HF. The amount of oil in the wax, however, must fall within a particular range as previously described, if this enhanced VI phenomenon is to be obtained.

55 A meshed platinum on fluorided alumina catalyst (Catalyst 1 from Example 1) was used to isomerize a slack wax obtained from 600N oil. The wax samples had oil contents of <1%, about 7% and about 23%. The wax containing less than about 1% oil was made by recrystallizing a 600N slack wax by warm-up decouling then hydrotreating. This 1% oil wax has 99% saturates, 0.8% aromatics and 0.2% polar compounds (as determined by silica gel separation). It had an initial boiling point of 382°C and a 99% off

boiling point of 588°C, as determined by GCD. Subsequently, isomerized products were dewaxed to between -18 to -21°C pour. Fractionation of the products showed that at the higher viscosity range the isomerate made from wax possessing about 7% oil exhibited an unexpected VI enhancement as compared to the other wax samples having <1% and 23% oil. This is to be compared with the results obtained using an extrudate $\text{Pt}/\text{FA}_2\text{O}_3$ catalyst.

6 Comparison Catalyst 4 was used to isomerize slack waxes obtained from 600N oil, which slack waxes contained <1%, 10.9% and 22% oil under conditions selected to achieve the levels of conversion indicated in Table 7. Comparing the results obtained using Catalyst 1 with those obtained using Comparison Catalyst 4 one sees that isomerization utilizing the meshed catalyst (Catalyst 1) exhibits an unexpected VI

10 enhancement when the wax feed employed contains about 7% oil.
From the above it is clear that the sized catalyst is preferred for use in the isomerization process described herein. Reference to Figure 3 shows that Catalyst 1 has the highest selectivity for oil production making it a preferred catalyst (Catalyst I of the Figure).

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TABLE 7

Example of Unexpected VI Enhancement using
Meshed Catalyst on Wax Containing ~ 10% oil

Catalyst	Oil Content of Wax	Conv. to 370C-	Vis. @ 100°C	VI
	<1	13	4.8	148
	7	24	4.8	150
1	23	12.8	4.8	135
	23	25.8	4.8	137
	<1	19.3	4.8	147
		35.0	4.6	142
	10.9	26.8	4.9	141
Comparison Cat 4	22	28.8	5.0	139
		48.6	4.6	136

Example 7

Slack wax from Bright Stock containing 15% oil was hydrotreated over Cyanamid's HDN-30 catalyst at 399°C, 0.5 v/v/h, 1000 psi H₂ and 1500 SCF/B, H₂, yielding a hydrotreated slack wax with the following properties:

Wax Oil content: 22.8 wt%
Sulfur = 3ppm
Nitrogen = < 1ppm

Distillation Data	
GCD % off at °C. ibp,255	
10	363
20	436
30	481
40	515
50	541
60	564
70	590
80	656

The hydrotreated slack wax was then isomerized over Catalyst 1 described in Example 1 to produce the following isomerate products:

Isomerization Conditions:	Run 1	Run 2
Temperature, °C	332	332
Pressure psi H ₂	1000	1000
Gas rate SCF/B, H ₂	5000	5000
LHSV (v/v/h)	0.9	0.9

Isomerate Product	A	B
Max 370°C Dewaxed oil yield (wt% on feed) (by ASTM D3235 method)	54.6	54.9
Conversion to 370°C ⁻ (wt% on feed)	28.4	27.6

The isomerate products A and B made from the Bright Stock slack wax were fractionated into a broad heart cut (from product A) and a narrow cut (from product B) and dewaxed using MEK/MIBK under conventional dilution chilling dewaxing conditions. This was a DILCHILL dewaxing operation run at 150 cm/sec. agitation top speed (2 inch agitator) at an outlet temp. of -13°C. Indirect chilling was then employed to get down to the filter temperature. From review of the data presented in Tables 8 and 8A it is apparent that fractionating the isomerate into a heart cut boiling between 370-582°C not only facilitated dewaxing the oil to the target pour point but permitted the dewaxing to be more efficient (i.e. higher filter rates) than with the narrow fraction. Higher yields of oil were obtained at good dewaxed oil filter rates on the broad heart cut as compared to narrow cut or 370°C topped fractions dewaxed under the same conditions. (Compare runs 1 and 2 Table 8 with runs A, B and I, Table 8A). This shows the advantage of dewaxing the heart cut when dealing with isomerate obtained from very heavy, high boiling wax fractions since operating on the heart cut permits dewaxing to be conducted under miscible conditions. Only when dealing with a broad heart cut can low pour points, high yields and good filter rates be simultaneously achieved.

TABLE 8
COMPARISON OF NARROW VERSUS BROAD HEAT CUT UTILIZATION
DURING DEWAXING PERFORMANCE FOR BRITISH STOCK ISOMERATES

Isomeric Rolling Range, °C:	1	2	3	4	5	6
Deaxing Conditions:						
Solvent Type:	M/R/M/R	M/R/M/R	M/R/M/R	M/R/M/R	M/R/M/R	M/R/M/R
Solvent Ratio, V/V	10/9	20/80	20/80	20/80	30/70	0/100
Mixing, Solv/Feed, V/V		4.3	4.1	4.1	4.3	-
Filter Temperature, °C	-25	-25	-30	-35	-35	-25
Miscibility	Miscible	Miscible	Borderline	Immiscible	Immiscible	Miscible
Feed Filter Rate, M/M2 Day	3.8	3.8	4.2	3.7	4.8	3.4
Wax Cake Liquids/Solids, W/W	7.7	9.4	8.4	10.5	10.5	8.3
Wash/Feed, W/W	-	1.0	1.1	1.0	0.88	-
Unconverted wax content, Wt %	22	42	37	56	66	33
Theoretical TMO yield, Wt %	-	21	23	25	25	21
(100-MC), wt %	73.1	63.8	63.5	43.2	26.5	68.7
Deaxed oil yield, wt %	2.8	7.5	2.5	1.6	1.3	2.3
Deaxed oil filter rate, M/M2 Day						
Deaxed oil inspection:						
Viscosity, cSt	25.5	25.30	25.75	24.49	22.67	25.7
at 40°C	5.31	5.28	5.34	5.15	4.87	5.34
at 100°C	147	147	147	146	143	147
Viscosity Index	-20	-20	-26	-32	-32	-20
Pour, °C	-17	-17	-22	-28	-31	-16
Cloud, °C						

6 10 15 20 25 30 35 40 45 50 55

TABLE 8A
COMPARISON OF NARROW VERSUS BROAD HEAVY CUT DILUTION
CHILLING DEMAXING PERFORMANCE FOR BRIGIT STOCK ISOMERATES

Isomerase Rolling Range, °C:	Narrow Cut 495-582						Topped 370°C ⁺	
Run	A	B	C	D	E	I		
Deaxing Conditions:								
Solvent Type:	MEK/MIBK	MEK/MIBK	MEK/MIBK	MEK/MIBK	MEK/MIBK	MEK/MIBK		
Solvent Ratio, V/V	10/90	20/80	30/70	0/100	5/95	10/90		
Dilution, Ratio, Solv/Feed, V/V	4.3	4.5	3.9	-25	-25	4.2		
Filter Temperature, °C	-25	-25	-25	-25	-25	-25		
Miscibility	Miscible/ borderline	Immiscible	Immiscible	Miscible	Borderline	Miscible/ borderline		
Feed Filter Rate, M3/M2 Day	3.2	1.8	6.6	3.1	3.0	2.9		
Wax Cake Liquids/Solids, V/W	5.1	6.9	6.8	6.1	5.6	5.9		
Wash/Feed, W/W	1.19	1.08	0.87	-	-	24		
1 oil in Wax	18	52	62	-	-	28		
Wax Content, wt. %	29	29	30	-	-	72		
Theoretical, nmo Yield, (100-WC), wt %	71	71	70	-	-	-		
Deaxed oil yield, wt. %	64.6	39.6	21.1	65.3	65.8	63.2		
Deaxed oil filter rate,	2.1	1.5	1.4	2.0	2.0	1.8		
M3/M2 Day								
Deaxed oil inspections:								
Viscosity, cSt	56.1	51.3	49.6	48.7	53.6	34.9		
@ 40°C	9.18	8.83	8.63	8.37	9.13	6.63		
@ 100°C	145	152	152.5	148	152	148		
Viscosity Index	-20	-21	-22	-15	-15	-20		
Pour, °C	-15	-14	-17	-	-	-18		
Cloud, °C								

55 Example 8

Slack wax derived from a 800N oil was hydrotreated over KF-840, a Ni/Mo on alumina hydrotreating catalyst at 370 °C, 0.33 LHSV, 1500 SCF H₂/bbl, 1000 psi H₂. The hydrotreated wax had a sulfur content of

6 wppm, a nitrogen content of <1 wppm, an oil content of 18.7 wt%, an initial boiling point of 233°C and a 95% off boiling point of 338°C.

The slack wax was isomerized over Catalyst 2 in three runs at high mass velocity as described in Table 9.

Table 9

	Run 1	Run 2	Run 3
Pressure (psi)	1200	1200	1200
LHSV	1.0	1.0	1.0
gas rate SCF/bb,H ₂	2500	2500	2500
Temp °C	329	328.9	327.1
Yield (wt%)			
370°C ⁻	37.5	37.8	22.0
Max 370°C ⁺ Oil*	49.8	50.5	52.5
residual wax	12.7	11.8	25.5

* Oil yield determined using ASTM D-3235 test method

Isomerate from these three runs was combined to produce a feed to the dewaxer having a 370°C⁻ wt% on feed of 26.6. The feed was fractionated into a 370°C⁺ fraction and 420°C⁺ fraction and dewaxed under simulated DILCHILL conditions in the laboratory using the procedure described in Example 7. DILCHILL dewaxing was performed using two different solvent systems on the two above described fractions. The results are presented in Table 10, below:

Table 10
MILCHILL Dewatering of 600 Neutral Slack Wax Isomerates
Comparison of Two Solvent Systems

Isomerate Fraction, °C	370°C		420°C+	
	MEK/MIBK 20/80	MEK/Toluene 50/50	MFK/MIBK 20/80	MEK/Toluene 50/50
Solvent Composition, v/v	49	49	52	52
Feed Cloud, °C	5.2	5.2	5.2	5.2
Viscosity, cst @ 100°C	<u>-27</u> 27.4	<u>-30</u> 26.4	<u>-27</u> 30.5	<u>-30</u> 29
Filter Temp. °C				
Wt. % Wax Removed				
Dewaxed Oil Properties				
Pour, °C	<u>-24</u> -20	<u>-21</u> -18	<u>-24</u> -21	<u>-21</u> -18
Cloud, °C	3	9	3	9
Pour-Filter dt, °C	7	12	6	12
Cloud-Filter dt, °C				
Viscosity, cst @ 40°C	72.9	23.2	28.5	28.9
Viscosity, cst @ 100°C	4.92	4.94	5.68	5.72
Viscosity Index	144	144	143	144
Feed Filter Rate, m ³ /m ² , day	4.7	4.4	5.3	4.7
Max Cake Liquids/ Solids, v/v	6.8	7.3	5.8	6.1
Dewaxed Oil Filter rate m ³ /m ² day	2.9	2.7	2.9	2.7

Average Solvent/Feed dilution on all runs was 3.4 v/v on feed.

From this it can be seen that to achieve extremely low pour points, it is preferred to use MEK/MIBK as the dewaxing solvent.

NOTES

- Temperature in °F is converted to equivalent °C by subtracting 32 and then dividing by 1.8.
- Length in inch(") is converted to cm by multiplying by 2.54.
- 1 SCF = 28.316 liter.
- 1 B = 159.0 liter.
- Pressure in psi is converted to equivalent kPa by multiplying by 6.895.
- Mesh sizes are of the Tyler series.

Reference is made to the following copending applications:

- 10 EP-A-321298 (EP patent application No. 88311978.8) describes and claims a method of producing a lube oil base stock or blending stock comprising the step of contacting a slack wax with an isomerization catalyst under isomerization conditions, wherein the catalyst comprises a fluorided hydrogenation metal-loaded refractory oxide, characterized in that the slack wax feed has a sulfur content not exceeding 20 ppm and nitrogen content not exceeding 5 ppm (of the wax feed) and the catalyst is in the form of particles having sizes of about $1/32$ inch and less (i.e., about 0.79375 mm and less) across their largest cross-sectional dimensions. The isomerization catalyst particles may be made by either (a) depositing at least one Group VIII metal on a particle extrudate refractory metal oxide support, fluoriding the metal-loaded support using hydrogen fluoride solution, and crushing the fluorided metal-loaded support to expose inner surfaces thereof and recovering sized material having particle sizes of about $1/32$ inch and less (i.e., about 0.79375 mm and less) across their largest cross-sectional dimensions, or (b) depositing at least one Group VIII metal on a particle extrudate refractory metal oxide support having particle sizes of about $1/32$ inch and less (i.e., about 0.79375 mm and less) across their largest cross-sections and fluoriding the metal-loaded support using a hydrogen fluoride solution, and for the particles of fluorided metal-loaded support made by the steps (a) or (b), activating the resulting particles of fluorided metal-loaded support by heating to a temperature in the range of from 350 to 500 °C in a hydrogen atmosphere for a time of from 1 to 48 hours or more.

- EP-A-321302 (EP patent application No. 88311983.6) discloses and claims a method for producing lube oil base stocks or blending stocks from waxy feed comprising the step of contacting the feed with a wax-isomerization catalyst under isomerization conditions, wherein the said catalyst comprises a hydrogenation metal-loaded fluorided alumina or material containing-alumina catalyst and which catalyst, as introduced to waxy feed, is characterized by possessing (1) a hydrate level of 60 or less as determined as the relative amount of hydrate represented by a peak in the X-ray diffraction (XRD) pattern at $2\theta = 5.66^\circ$ (0.566 nm) when a hydrate level of 100 corresponds to the $2\theta = 5.66^\circ$ (0.566 nm) peak height exhibited in the XRD by a standard material constituting 0.6 wt% Pt on 150 m²/g gamma-alumina containing 7.2 wt% fluorine wherein the fluorine has been deposited using an aqueous solution containing a high concentration of HF and the material dried at 150 °C for 16 hours; (2) a surface nitrogen content N/AI ratio of 0.01 or less as determined by X-ray photo-electron spectroscopy; (3) a bulk fluorine concentration of between from 2 to 10 wt% and (4) a surface fluorine concentration defined as the amount of fluorine present in a layer between the surface of the catalyst to a depth of about $1/100$ inch (0.254 mm) of less than about 3 wt% provided that the surface fluoride concentration is less than the bulk fluoride concentration.

- 40 EP-A-321303 (EP patent application No. 88311984.4) discloses and claims a process for producing middle distillate fuel products from a paraffin wax which process comprises (a) contacting the wax with hydrogen in a hydroisomerization zone (R-1) at hydroisomerization conditions in the presence of a fluorided Group VIII metal-on-alumina catalyst and converting from 50 to 95 weight percent therein of the 700 °F + (371 °C) material present in the wax; said catalyst having (i) a bulk fluoride concentration in the range of from 2 to 10 weight percent (e.g. 5 to 8 weight percent), wherein the fluoride concentration is less than about 3.0 weight percent (e.g. less than 1.0 weight percent, preferably less than 0.5 weight percent) at the outer surface layer to a depth less than one one-hundredth of an inch (0.254 mm), provided the surface fluoride concentration is less than the bulk fluoride concentration; (ii) an aluminum fluoride hydroxide hydrate level greater than 60 (where an aluminum fluoride hydrate level of 100 corresponds to the X-ray diffraction peak height at 5.66° (0.566 nm) for a Reference Standard containing 0.6 weight percent Pt and 7.2 weight percent F on gamma alumina having a surface area of about 150 m²/g and which is prepared by treatment of standard reforming grade platinum-on-alpha-alumina material containing 0.6 weight percent Pt on 150 m²/g surface area gamma alumina by single contact with an aqueous solution of hydrogen fluoride (e.g., 10-15 weight percent HF solution, such as 11.6 weight percent HF solution) with drying at 150 °C for 16 hours; and (iii) a N/AI ratio less than about 0.005 (e.g. less than 0.002), and (b) recovering (D-2) a middle distillate product and a bottoms product having an initial boiling point above 700 °F (371 °C).

EP-A-321305 (EP patent application No. 88311886.9) discloses and claims a process for producing a pumpable syncrude from a Fischer-Tropsch wax containing oxygenate compounds, which comprises:

- (1) separating (D-O) the Fischer-Tropsch wax into (a) a low-boiling fraction which contains most of the oxygenate compounds and (b) a high-boiling fraction which is substantially free of water and oxygenate compounds,
- (2) reacting (R-1) the high-boiling fraction from step (1) with hydrogen at hydroisomerization and mild hydrocracking conditions in the presence of a fluorided Group VIII metal (e.g., platinum)-on-alumina catalyst to produce a C_5 + hydrocarbon product, and
- (3) combining the C_5 + hydrocarbon product from step (2) with the low-boiling fraction from step (1) to produce a pumpable, refinery-processable syncrude that can be transported at atmospheric conditions.

EP-A-321306 (EP patent application No. 88311887.7) discloses and claims a method for improving the yield of oil boiling in the lube oil base stock or blending stock range produced by the isomerization of wax over an isomerization catalyst, comprising conducting the wax isomerization procedure over a catalyst comprising or consisting of palladium on fluorided alumina or fluorided alumina containing support material.

EP-A-321304 (European patent application No. 88311885.1) describes and claims the use for producing an improved yield of lube oil in the viscosity grade 5.6 to 5.9 cSt (5.6 to 5.9 mm²/s) at 100 °C from an isomerized wax of a method comprising (1) isomerizing wax over an isomerization catalyst comprising a Group VI metal, Group VIII metal and mixtures deposited on a halogenated refractory metal oxide support under isomerization conditions including a temperature in the range of from 270 to 400 °C, a pressure in the range of from 500 to 3000 psi (3.45 to 20.60 MPa) H_2 and a space velocity in the range of from 0.1 to 10 v/v/hr, but at a low treat gas rate in the range of from 500 to 5000 SCFH₂/bbl (89.05 to 890.53 liter H_2 gas/liter oil), and (2) fractionating the isomerate to recover a lube fraction boiling in the range 330 °C + from which oil in the viscosity grade 5.6 to 5.9 cSt (5.6 to 5.9 mm²/s) at 100 °C is recovered after dewaxing.

EP-A-323092 (EP patent application No. 88311982.8) discloses and claims a process for producing a lubricating oil having a high viscosity index and a low pour point from a Fischer-Tropsch wax, which process comprises:

- (a) contacting the Fischer-Tropsch wax with a hydrotreating catalyst (which may be unsulfided) and hydrogen in a hydrotreating zone (R-1) under hydrotreating conditions (comprising a temperature in the range 650 to 775 °F (343.3 to 412.8 °C), a hydrogen pressure in the range 500 to 2500 psig (3.448 to 17.238 MPa), a space velocity in the range 0.1 to 2.0 v/v/h and a hydrogen to feed rate in the range 500 to 5000 SCF/B (89.04 to 890.44 liters H_2 per liter feed)) to reduce the oxygenate and trace metal levels of the wax and to partially hydrocrack and isomerize the wax;
- (b) contacting the hydrotreated Fischer-Tropsch wax from step (a) with hydrogen under hydroisomerization conditions (comprising a temperature in the range of from 500 to 750 °F (260 to 398.9 °C), a feed space velocity in the range of from 0.2 to 2.0 v/v/h, a gauge pressure in the range of from 500 to 2500 psig (3.448 to 17.238 MPa) and a hydrogen feed rate in the range of from 500 to 10,000 SCF/B (89.04 to 178.88 liters H_2 /liter feed)) in a hydroisomerization zone (R-2) in the presence of a fluorided Group VIII metal-on-alumina catalyst having (i) a bulk fluoride concentration ranging from 2 to 10 weight percent, wherein the fluoride concentration is less than about 3.0 weight percent at the outer surface layer to a depth less than one one-hundredth of an inch (0.254 mm), provided the surface fluoride concentration is less than the bulk fluoride concentration, (ii) an aluminum fluoride hydroxide hydrate level greater than 60 (e.g., at least about 100) where an aluminum fluoride hydrate level of 100 corresponds to the X-ray diffraction peak height of 5.86 Å (0.566 nm) for a Reference Standard containing 0.6 wt.% Pt and 7.2 wt.% F on a support of gamma-alumina having a surface area of about 150 m²/g and which Reference Standard is prepared by treating standard reforming grade gamma alumina having a surface area of about 150 m²/g with platinum followed by single contact with an aqueous solution containing a high concentration of hydrogen fluoride followed by drying at about 300 °F (148.9 °C) and (iii) a N/AI ratio less than about 0.005;

EP-A-3237224 (EP patent application No. 88311888.5) discloses and claims a method for improving the daylight stability of a lube oil base stock or blending stock produced by the isomerization of wax, said method comprising hydrotreating either (a) the total liquid product produced in the wax isomerization unit or (b) the lube boiling range fraction of the isomerate, said hydrotreating employing a catalyst selected from Group VIII metal on refractory metal oxide and Group VIII metal on halogenated refractory metal oxide, a temperature in the range of from 170 to 270 °C, a flow velocity of from 0.25 to 10 v/v/hr., a pressure of from 300 to 1500 psi (2.069 to 10.343 MPa) H_2 and a hydrogen gas rate of from 500 to 10,000 SCF/B (89.05 to 1780.94 liters gas/liter oil).

Claims

- # Claims
1. A process for producing lube oil base stocks or blending stocks having a pour point of -20°C or lower and a viscosity index of 130 and higher by the isomerization of wax, said process comprising the steps of (1) isomerizing the wax in an isomerization unit over an isomerization catalyst to a level of conversion such that from 15 to 35% unconverted wax, calculated as (unconverted wax)/(unconverted wax + dewaxed oil) $\times 100$, remains in the fraction of the isomerate boiling in the lube boiling range sent to the dewaxing unit, wherein the catalyst contains a hydrogenating metal (e.g., Group VI and/or Group VIII) component supported on a halogenated (e.g., fluorided) refractory metal oxide (e.g., alumina), and the isomerization conditions comprise a temperature in the range of from 270 to 400°C , a pressure of from 500 to 3000 psi (3.45 to 20.69 MPa) H_2 , a gas rate of 1000 to 10,000 SCF/b (178.1 to 1780.9 liter gas/liter oil), and a space velocity in the range 0.1 to 10 v/v/hr, fractionating the total product from the isomerization zone into a lube fraction boiling in the 330°C - 800°C temperature range; (2) solvent dewaxing said fraction in a single solvent dewaxing step wherein the wax separation temperature is in the range of from -25 to -35°C ; and (3) recovering a lube oil product having a VI of at least 130 and a pour point of -20°C or lower.
 2. The process of claim 1 wherein the wax separation temperature in the solvent dewaxing step is in the range of from -25 to -30°C .
 3. The process of claim 1 or claim 2 wherein the level of conversion is from 20 to 30% unconverted wax.
 4. The process of any one of claims 1 to 3 comprising recovering a lube oil product having a pour point of -21°C or lower in step (3).
 5. The process of any one of claims 1 to 4 wherein the wax which is fed to the isomerization unit is a slack wax which has been hydrotreated so as to contain about 1 to 5 ppm nitrogen, about 1 to 20 ppm sulfur and has been deoiled to contain 0 to 35 wt% oil.
 6. The process of any one of claims 1 to 5 wherein the isomerate from the isomerization zone is fractionated into a lube oil fraction boiling in the 370 - 580°C range.
 7. The process of any one of claims 1 to 6 wherein the solvent dewaxing step is practiced using C_3 - C_6 ketones, C_6 - C_{10} aromatic hydrocarbons, mixtures of C_3 - C_6 ketones, mixtures of C_3 - C_6 ketones and aromatic hydrocarbons, liquified, normally gaseous C_2 - C_4 hydrocarbons.
 8. The process of any one of claims 1 to 7 wherein the solvent dewaxing step is practiced using a mixture of methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) in a ratio of 20/80 at a temperature in the range -25 to -30°C .
 9. The process of any one of claims 1 to 7 wherein the solvent dewaxing step is practiced using methylisobutyl ketone.
 10. The process of any one of claims 1 to 9 wherein unconverted wax recovered in the dewaxing step and/or the fraction boiling above 600°C is recycled to be further isomerized.

Patentansprüche

- Patentansprüche**
1. Verfahren zur Herstellung von Schmierölgrundmaterialien oder -mischmaterialien, die einen Stockpunkt von -20 °C oder darunter und einen Viskositätsindex (VI) von 130 und darüber aufweisen, durch die Isomerisierung von Paraffin, wobei das Verfahren Stufen umfaßt, in denen
- (1) das Paraffin in einer Isomerisierungsanlage über einem Isomerisierungskatalysator bis zu einem solchen Umwandlungsgrad isomerisiert wird, daß 15 bis 35 % nicht umgewandeltes Paraffin, berechnet als (nicht umgewandeltes Paraffin)/(nicht umgewandeltes Paraffin + entparaffiniertes Öl) x 100, in der Fraktion des im Schmierölbereich siedenden Isomerisats verbleiben, das zu der Entparaffinierungsanlage geleitet wird, wobei der Katalysator eine Hydriermetallkomponente (z. B. Gruppe VI und/oder Gruppe VIII), die auf einen Träger aus halogeniertem (z. B. fluoriertem) feuerfesten Metalloxid (z. B. Aluminiumoxid) aufgebracht ist, enthält und die Isomerisierungsbedin-

- gungen eine Temperatur im Bereich von 270 bis 400 °C, einen Druck von 500 bis 3 000 psi (3,45 bis 20,69 MPa) H₂, eine Gasgeschwindigkeit von 1 000 bis 10 000 SCF/b (178,1 bis 1 780,9 Liter Gas/Liter Öl) und eine Raumgeschwindigkeit im Bereich von 0,1 bis 10 Vol./Vol./Std. umfassen, wobei das Gesamtprodukt aus der Isomerisierungszone in eine Schmierstofffraktion, die im Temperaturbereich von 330 °C bis 600 °C siedet, fraktioniert wird;
- 6 (2) diese Fraktion in einer einzigen Lösungsmittelentparaffinierungsstufe lösungsmittelentparaffiniert wird, wobei die Paraffintrennungstemperatur im Bereich von -25 °C bis -35 °C liegt und
- (3) ein Schmierölprodukt, das einen VI von mindestens 130 und einen Stockpunkt von -20 °C oder darunter aufweist, gewonnen wird.
- 10 2. Verfahren nach Anspruch 1, bei dem die Paraffintrennungstemperatur in der Lösungsmittelentparaffinierungsstufe im Bereich von -25 bis -30 °C liegt.
3. Verfahren nach Anspruch 1 oder Anspruch 2, bei dem der Umwandlungsgrad 20 bis 30 % nicht
- 15 umgewandeltes Paraffin beträgt.
4. Verfahren nach einem der Ansprüche 1 bis 3, bei dem in Stufe (3) ein Schmierölprodukt gewonnen wird, das einen Stockpunkt von -21 °C oder darunter aufweist.
- 20 5. Verfahren nach einem der Ansprüche 1 bis 4, bei dem das Paraffin, das in die Isomerisierungsanlage eingespeist wird, ein Rohparaffin ist, das wasserstoffbehandelt worden ist, so daß es etwa 1 bis 5 ppm Stickstoff und etwa 1 bis 20 ppm Schwefel enthält, und entölt worden ist, so daß es 0 bis 35 Gew.% Öl enthält.
- 25 6. Verfahren nach einem der Ansprüche 1 bis 5, bei dem das Isomerisat aus der Isomerisierungszone in eine Schmierölfraktion, die im Bereich von 370 bis 580 °C siedet, fraktioniert wird.
7. Verfahren nach einem der Ansprüche 1 bis 6, bei dem die Lösungsmittelentparaffinierungsstufe unter Verwendung von C₃ bis C₆-Ketonen, C₆ bis C₁₀-aromatischen Kohlenwasserstoffen, Mischungen aus
- 30 C₃ bis C₆-Ketonen, Mischungen aus C₃ bis C₆-Ketonen und aromatischen Kohlenwasserstoffen sowie verflüssigten, normalerweise gasförmigen C₂ bis C₄-Kohlenwasserstoffen durchgeführt wird.
8. Verfahren nach einem der Ansprüche 1 bis 7, bei dem die Lösungsmittelentparaffinierungsstufe unter Verwendung einer Mischung aus Methyläthylketon (MEK) und Methylisobutylketon (MIBK) in einem
- 35 Verhältnis von 20/80 bei einer Temperatur im Bereich von -25 bis -30 °C durchgeführt wird.
9. Verfahren nach einem der Ansprüche 1 bis 7, bei dem die Lösungsmittelentparaffinierungsstufe unter Verwendung von Methylisobutylketon durchgeführt wird.
- 40 10. Verfahren nach einem der Ansprüche 1 bis 9, bei dem nicht umgewandeltes Paraffin in die Entparaffinierungsstufe und/oder die Fraktion, die oberhalb von 600 °C siedet, rückgeführt wird, um weiter isomerisiert zu werden.

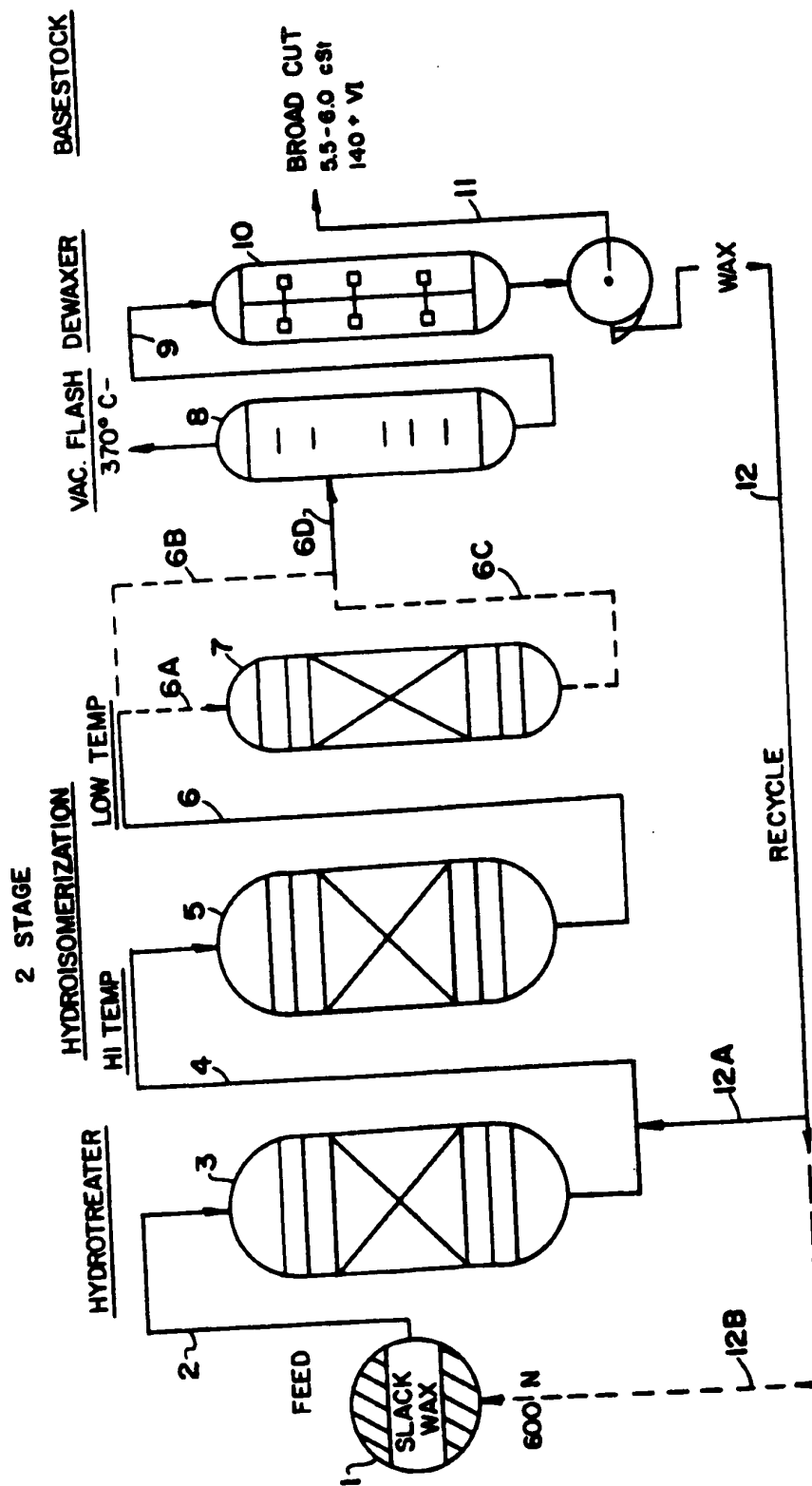
Revendications

- 45 1. Procédé pour la préparation de matière premières ou de matières de mélange d'huiles lubrifiantes, ayant un point d'écoulement de -20 °C ou moins et un indice de viscosité de 130 et plus, par isomérisation de paraffine, ledit procédé comprenant les étapes de (1) isomérisation de la paraffine,
- 50 isomérisation de paraffine, ledit procédé comprenant les étapes de (1) isomérisation de la paraffine, dans une unité d'isomérisation, sur un catalyseur d'isomérisation, jusqu'à un taux de conversion tel que de 15 à 35 % de paraffine non convertie, calculés en (paraffine non convertie)/(paraffine non convertie + huile déparaffinée) x 100, restent dans la fraction du produit d'isomérisation bouillant dans le
- domaine d'ébullition du lubrifiant, envoyé à l'unité de déparaffinage, le catalyseur contenant un composant à base d'un métal (par exemple du groupe VI et/ou du groupe VIII) hydrogéné fixé sur un
- oxyde métallique réfractaire (l'alumine par exemple) halogéné (par exemple fluoré), et les conditions
- 55 d'isomérisation comprenant une température dans la plage allant de 270 à 400 °C, une pression de H₂ allant 3,45 à 20,69 MPa (500 à 3 000 psi), un débit de gaz allant de 178,1 à 1 780,9 litres de gaz par litre d'huile [1 000 à 10 000 SCF/b (pieds cubes/baril)] et une vitesse spatiale dans la plage allant de 0,1 à 10 v/v/h, fractionnement du produit total, provenant de la zone d'isomérisation, en une fraction

- lubrifiante bouillant dans la plage de températures allant de 330 à 600 ° C; (2) déparaffinage, à l'aide d'un solvant, de ladite fraction en une seule étape de déparaffinage par solvant dans laquelle la température de séparation de la paraffine est dans la plage allant de -25 à -35 ° C; et (3) récupération d'un produit de type huile lubrifiante ayant un indice de viscosité d'au moins 130 et un point d'écoulement de -20 ° C ou moins.
2. Produit selon la revendication 1, dans lequel la température de séparation de paraffine, dans l'étape de déparaffinage par solvant, est dans la plage allant de -25 à -30 ° C.
 3. Procédé selon la revendication 1 ou 2, dans lequel le taux de conversion est de 20 à 30 % de paraffine non convertie.
 4. Procédé selon l'une quelconque des revendications 1 à 3, comprenant la récupération d'un produit de type huile lubrifiante ayant un point d'écoulement de -21 ° C ou moins dans l'étape (3).
 5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel la paraffine envoyée à l'unité d'isomérisation est une paraffine brute qui a été hydrotraitée de manière à contenir d'environ 1 à 5 ppm d'azote, d'environ 1 à 20 ppm de soufre, et a été déshuilée pour contenir de 0 à 35 % en poids d'huile.
 6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel le produit d'isomérisation provenant de la zone d'isomérisation est fractionné en une fraction d'huile lubrifiante bouillant dans la plage allant de 370 à 580 ° C.
 7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel l'étape de déparaffinage par solvant est effectuée au moyen de cétones en C₃-C₆, d'hydrocarbures aromatiques en C₆-C₁₀, de mélanges de cétones en C₃-C₆, de mélanges de cétones en C₃-C₆ et d'hydrocarbures aromatiques et d'hydrocarbures en C₂-C₄ liquéfiés normalement gazeux.
 8. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel l'étape de déparaffinage par solvant est effectuée au moyen d'un mélange de méthyléthylcétone (MEK) et de méthylisobutylcétone (MIBK) en un rapport de 20:80, à une température dans la plage de -25 à -30 ° C.
 9. Procédé selon l'une quelconque des revendications 1 à 7, dans lequel l'étape de déparaffinage par solvant est effectuée au moyen de méthylisobutylcétone.
 10. Procédé selon l'une quelconque des revendications 1 à 9, dans lequel la paraffine non convertie, recueillie dans l'étape de déparaffinage, et/ou la fraction bouillant au-dessus de 600 ° C, est recyclée pour être isomérisée davantage.

SLACK WAX ISOMERIZATION PROCESS FOR SINGLE FEED / BASESTOCK

FIG.1



SLACK WAX ISOMERIZATION PROCESS

FIG. 2

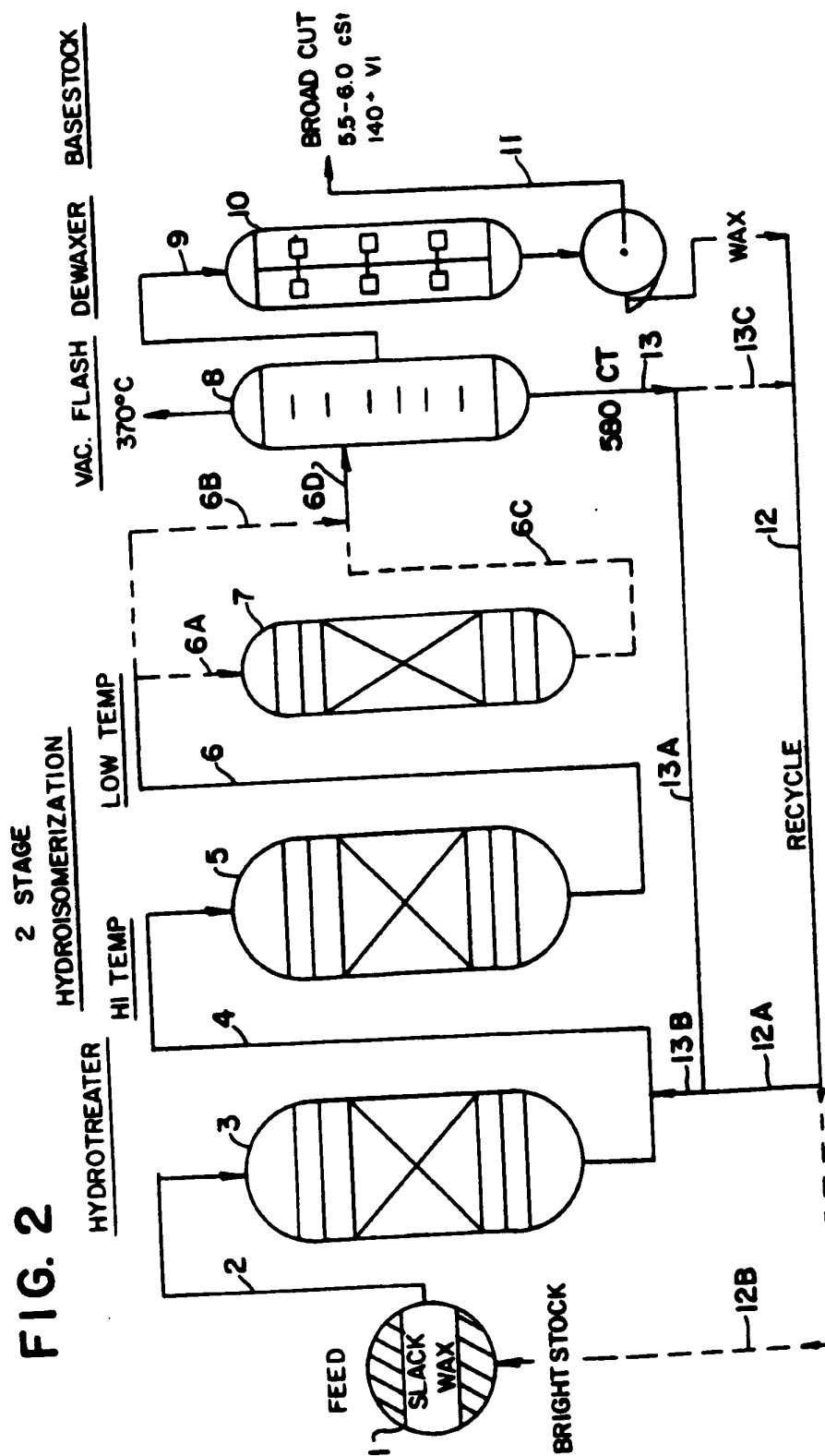


FIG. 3

